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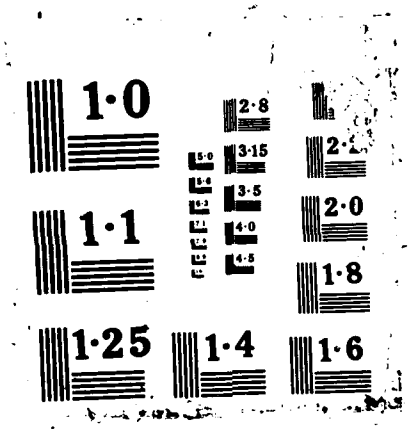
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REPORT DOCUMENTATION PAGE

AD-A192 394

	1b. RESTRICTIVE MARKINGS
SCHEDULE	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 21334.18-MS
6a. NAME OF PERFORMING ORGANIZATION University of Wisconsin-Milwaukee 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office
6c. ADDRESS (City, State, and ZIP Code) University of Wisconsin-Milwaukee Milwaukee, WI 53201	7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAG29-84-K-0126
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Near Ultraviolet-Visible-Near Infrared Optical Behavior of Sputter Deposited GeOx(1.85 < x < 2.30)

12. PERSONAL AUTHOR(S)
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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint	FROM _____ TO _____		

16. SUPPLEMENTARY NOTATION
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Abstract on reprint

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

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NEAR ULTRAVIOLET-VISIBLE-NEAR INFRARED OPTICAL BEHAVIOR OF SPUTTER DEPOSITED GeO_x ($1.85 \leq x \leq 2.30$)

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This paper describes the reactive sputter deposition and optical characterization of GeO_x where x lies between 1.85 and 2.30. The films were grown by sputtering a Ge target in O_2-bearing atmospheres containing 0 to 80% Ar. Films deposited in 0 to 60% Ar were nominally germania. However, transmission in the UV-visible, the strength of the 245nm defect center, the optical absorption coefficient, and the optical energy band gap were strongly influenced by the presence of Ar in the discharge. Films deposited in gas containing 80% Ar were substoichiometric germania.

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I. INTRODUCTION

This paper describes the near infrared-visible-near ultraviolet optical behavior of glassy GeO_x films where x lies between 1.85 and 2.30. The films were grown by reactive sputter deposition using a Ge cathode and rf-excited, O_2-bearing discharges containing 0 to 80% Ar.

Spectrophotometry was used to determine transmission and reflection characteristics from which the refractive index, the absorption coefficient, and the optical band gap were calculated. Chemical analysis using Rutherford backscattering spectroscopy was carried out. Combined optical and chemical data allowed conclusions to be drawn about atomic order in the films as a function of sputtering gas composition.

Germania was chosen to study because we want to increase our understanding of the growth of tetrahedral oxide glasses from the vapor phase. Many years have been devoted to investigating the atomic order, defect structure, and

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Proc. 2nd International Conference on the Effects of Modes of Formation on the Structure of Glasses, Vanderbilt University, Nashville, TN, June 1987

crystallization kinetics of fused germania (1-12). However, a solidification product from the melt may be very different from a material grown from a vapor, in particular by a deposition process involving exposure of the growth interface to a plasma. In contrast to the sizable body of literature on fused germania, there are few basic studies addressing any aspect of thin film growth and characterization.

II. EXPERIMENTAL PROCEDURE

FILM DEPOSITION:

A liquid nitrogen cold trapped, hot-oil diffusion pumped, rf-excited planar diode sputter deposition system was used to grow the films. The sputtering target was an 8 cm diameter, 99.9999% Ge disc which was bonded to a water-cooled Cu cathode. The substrates were Supersil fused quartz flats which had been chemically cleaned using a chelating procedure and placed in thermal contact with a water-cooled Cu anode. To prevent Cu contamination of the film by backsputtering of the anode, areas of the anode which were not covered by the substrates were coated with 100Å of Ge. The distance between target and substrate surface was 5 cm.

The chamber was evacuated to a pressure of $1x10^{-6}$ Torr and backfilled to $1x10^{-2}$ Torr with 99.999% pure Ar gas. The residual gas in the chamber before backfilling was H_2O. The target was sputter-cleaned for 45 min using a 300W Ar discharge with a shutter covering the substrates. The discharge was then extinguished, the chamber was re-evacuated and backfilled with a particular Ar-O_2 mixture or O_2 alone. O_2 of 99.97% purity was used for the depositions. Discharges containing 20, 40, 60, and 100% O_2 were investigated. The target was sputtered in the O_2-bearing atmosphere of choice for an additional 45 min before the shutter was opened and a film was deposited.

FILM CHARACTERIZATION:

Film thickness was determined using a profilometer to measure the height of a step produced by masking a region of the substrate during deposition. The instrument-related uncertainty in each measurement was ±100Å. The film growth rate was obtained by dividing film thickness by deposition time.

X-ray diffraction was used to determine whether there was long range atomic order in the films. None was detected. However, the possibility of microcrystallinity cannot be ruled out by this measurement.

Rutherford backscattering spectroscopy (RBS) was used to determine the relative atomic concentration of Ge and O in the films. An IonX Model 4175 analyzer equipped with 2 Mev He^{++} bombarding ions was used.

A Perkin-Elmer Model 330 UV-VIS-IR double-beam spectrophotometer with a specular reflection attachment was used to measure the transmission and reflectivity of near-normal incidence radiation in the 190-2000 nm wavelength region. In reflection mode, the instrument was calibrated using a protected Al mirror. All measurements were made in laboratory air at room temperature, within 12 h of deposition and again at 6 mo. No aging was observed.

When determining the absorption coefficient α, transmission data was taken in double-beam mode with a bare substrate in the reference beam path. In this manner, absorption by the quartz substrate although small (<10%) was subtracted from the data. For a sample of thickness x and reflectivity R, the transmission T through the film alone is given by (13):

$$T = [(1-R)^2 \exp(-\alpha x)]/[1-R^2 \exp(-2\alpha x)]. \quad (1)$$

The optical band gap, as discussed by Tauc (14), was determined from the relationship:

$$\alpha h\nu = A(h\nu - E_o)^2. \quad (2)$$

where $\alpha > 10^4$ cm^{-1} and $h\nu$ is the energy of the incident radiation.

In the region of high transmittance ($h\nu < E_o$), the index of refraction $n(\lambda)$ was determined from the position of adjacent interference fringe maxima at λ_1 and λ_2 on the transmission spectra using the relationship (13):

$$n(\lambda) = \{2x[(1/\lambda_1) - (1/\lambda_2)]\}^{-1} \quad (3)$$

III. RESULTS AND DISCUSSION

Table I records the discharge conditions, film thickness, growth rate, and O/Ge atomic concentration in the films. Film A is substoichiometric germania. Films B-F have an O/Ge atomic ratio which lies between 2.0 and 2.5 ($\pm$5%) and is independent of sputtering gas composition. There is sufficient O in Films B-F to fully form saturated Ge bonds. The local bonding unit is therefore assumed to be the $Ge-O_4$ tetrahedron.

Film color changes from red-brown (A) to very pale brown (B) to almost imperceptable pale brown (C) to clear (D, E, and F) as the Ar content of the gas is decreased from 80 to 0%.

Figure 1a shows the UV-visible transmission characteristics of the film+

substrate composite. Films B, C, and D, all nominally germania, show increased absorption in the film of a featureless tail which extends into the visible as the gas Ar content is increased from 0 to 60%. Transmittance in the 800-2000 nm range is >90% for Films B, C, and D, and not shown in Fig. 1. The IR behavior of Film A, $GeO_{1.85}$, is shown in Fig. 1b.

Figure 2 shows the near absorption edge behavior of Films B, C, D, E, and F. Data was taken relative to a bare substrate and represents absorption by the film alone. An absorption band at ∿245 nm is observed here. This band has been extensively studied in fused germania (1,2,4,6,9,12,15). Following Vergano and Uhlmann (6), and assigning the band to an F' center (O vacancy + two trapped e^-), the defect concentration was calculated using Smakula's relationship. The results are recorded in Table II.

TABLE I: Deposition Conditions and O/Ge Concentration for GeO_x Films

Film	Gas	Cathode Voltage (V)[a]	Film Thickness (nm)	Growth Rate (nm/min)	O/Ge Conc.
A	Ar-20%O_2	2200	1120	6.2	1.85
B	Ar-40%O_2	2100	1160	8.2	2.22
C	Ar-60%O_2	2100	850	4.7	2.30
D	100%O_2	2000	828	3.5	2.27
E	100%O_2	2000	430	3.6	2.00
F	100%O_2	2000	210	3.5	2.00[b]

a) peak-to-peak voltage required to maintain a 300W discharge.
b) measured by x-ray photoelectron spectroscopy.

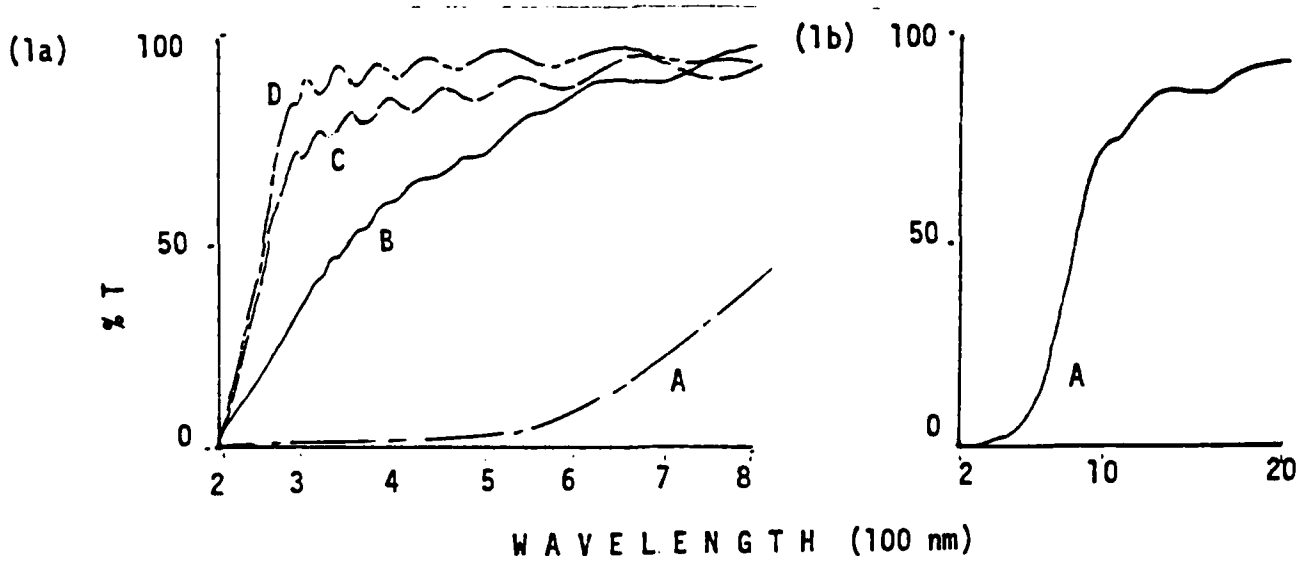

Fig 1: Transmittance through the film+substrate composite as a function of the wavelength of the incident radiation: Film A, Ar-20%O_2; Film B, Ar-40%O_2; Film C, Ar-60%O_2; Film D, 100%O_2.

The refractive index, calculated from Eq. (3) is shown in Fig. 3 as a function of the wavelength of incident radiation in the energy region $h\nu < E_o$. Included in Fig. 3 is a schematic drawing of the variation of $n(\lambda)$ with λ in the vicinity of an absorption band. The increase in $n(\lambda)$ for $\lambda \gtrsim$ 350 nm, that is, as the fundamental optical absorption edge is approached in Films C, D, and E, demonstrates this behavior. The bars in Fig. 3 are not error symbols, they represent the range of λ (λ_1-λ_2) over which the calculation was made.

TABLE II: Defect Concentration[a] and Optical Energy Band Gap of GeO_x Films.

Film	Gas	Defect Conc. (N/cm^3)	E_o (eV)	λ_o (nm)
A	Ar-20%O_2	-	1.1	1230
B	Ar-40%O_2	1.5×10^{18}	3.0	415
C	Ar-60%O_2	1.2×10^{19}	4.3	290
D	100%O_2	2.4×10^{18}	4.5	275
E	100%O_2	3.0×10^{18}	4.5	275
F	100%O_2	-	4.5	275

a) ± 35% error in measuring peak half width (Ref. 6).

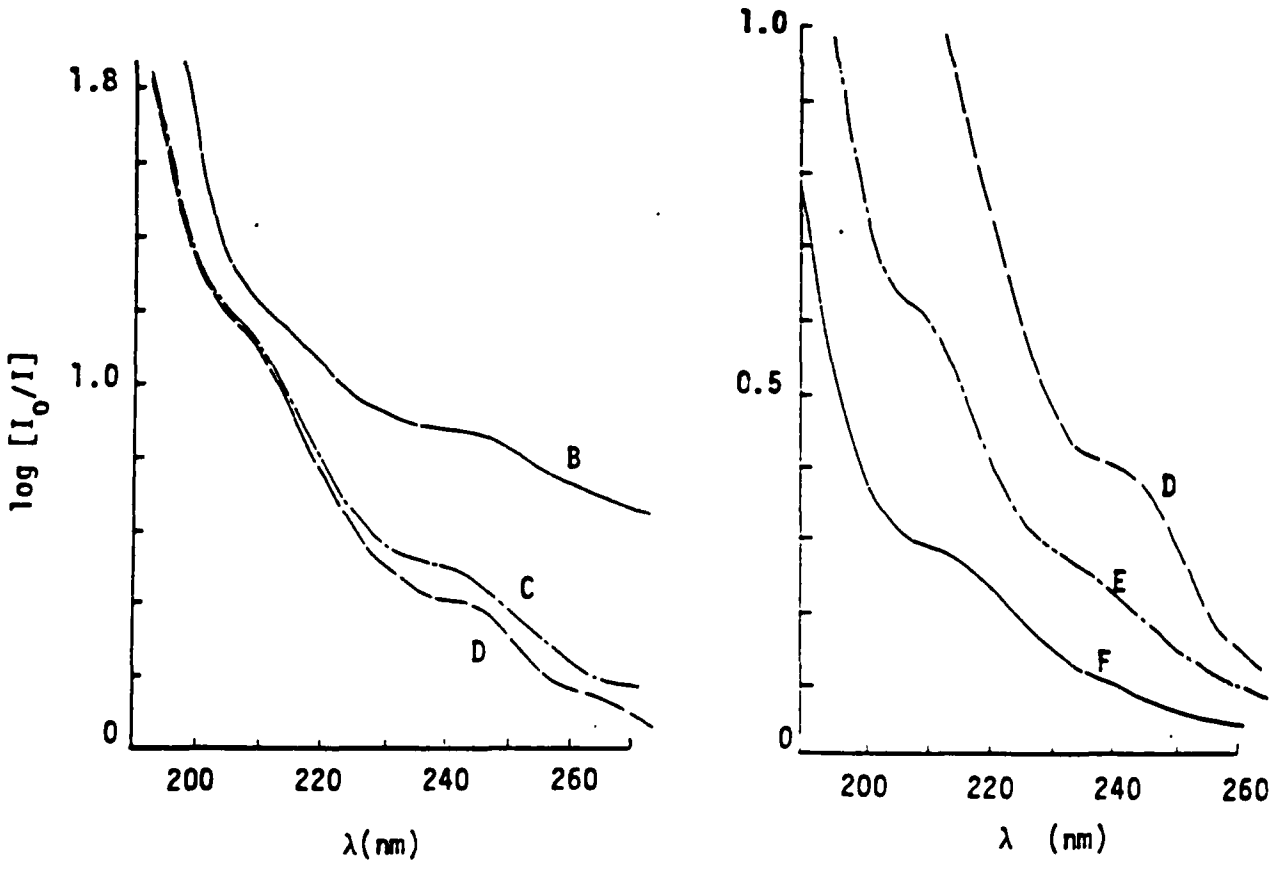

Fig. 2: Optical absorption as a function of the wavelength of the incident radiation.

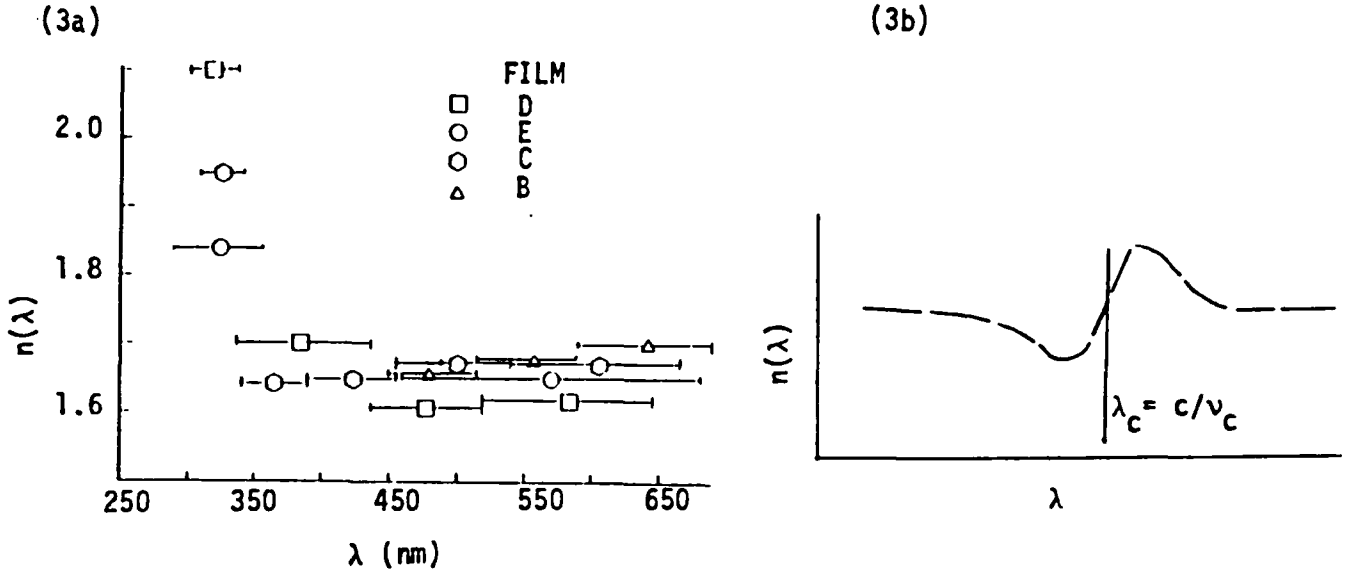

Fig. 3: a) The refractive index calculated from Eq. [3] for $[hc/\lambda]=[h\nu]<E_o$. b) The variation of $n(\lambda)$ with λ in the vicinity of an absorption band centered at λ_c.

The results presented above show the influence of Ar on the sputter deposition of films which are nominally germania (GeO_x where $2.0 \leq x \leq 2.3$). These effects include an increase in the UV-visible absorption and a decrease in the energy of the optical band gap as the Ar content of the sputtering gas is increased. No change in film chemistry accompanies these changes in optical behavior. These results are attributed to the disruption of $Ge-O_4$ bonding by Ar^+ bombardment of the growing film and will be the subject of further study.

ACKNOWLEDGEMENTS: We thank Drs. R.R. Reeber, R.A. Weeks, and M.G. Lagally for helpful discussions. This research was supported under ARO Grant No. DAAG 29-84-K-0126, ONR Contract No. N0014-86-K-0188, and NIH Grant No. RR01769.

REFERENCES:

(1) A.J. Cohen, Phys. Rev. 105, 1151 (1957).
(2) A.J. Cohen and H.L. Smith, J. Phys. Chem. Sol. 7, 301 (1958).
(3) J. Zarzychi and R. Mezard, Phys. Chem. Glasses 3, 163 (1962).
(4) R.A. Weeks and T. Purcell, J. Chem. Phys. 43, 483 (1965).
(5) T. Purcell and R.A. Weeks, Phys. Chem. Glasses, 10, 198 (1969).
(6) P.J. Vergano and D.R. Uhlmann, Phys. Chem. Glasses, 11, 30 (1970).
(7) P.J. Vergano and D.R. Uhlmann, Phys. Chem. Glasses, 11, 36 (1970).
(8) H. Bohm, Phys. Chem. Glasses 11, 177 (1970).
(9) E.J. Friebale, D.L. Griscom, and G.H. Sigel, Jr., J. Appl. Phys. 45, 3424 (1974).
(10) G. Kordas, R.A. Weeks, and D.L. Kinser, J. Appl. Phys. 54, 5394 (1983).
(11) R.H. Margruder III, D.L. Kinser, R.A. Weeks, and J.M. Jackson, J. Appl. Phys. 57, 345 (1985).
(12) J.M. Jackson, M.E. Wells, G. Kordas, D.L. Kinser, and R.A. Weeks, J. Appl. Phys. 58, 2308 (1985).
(13) J.I. Pankove, Optical Processes in Semiconductors (Prentice-Hall, New Jersey, 1971).
(14) J. Tauc and A. Menth, J. Non-cryst. Sol. 8-10, 569 (1972).
(15) V. Garino-Canina, J. Phys. Chem. Sol. 20, 110 (1961).

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